

Electronic Supplementary Information (ESI)

A fluorous-tag-assisted fluorescent probe for simple and selective detection of hydrogen sulfide: Application for turbid dyeing solutions

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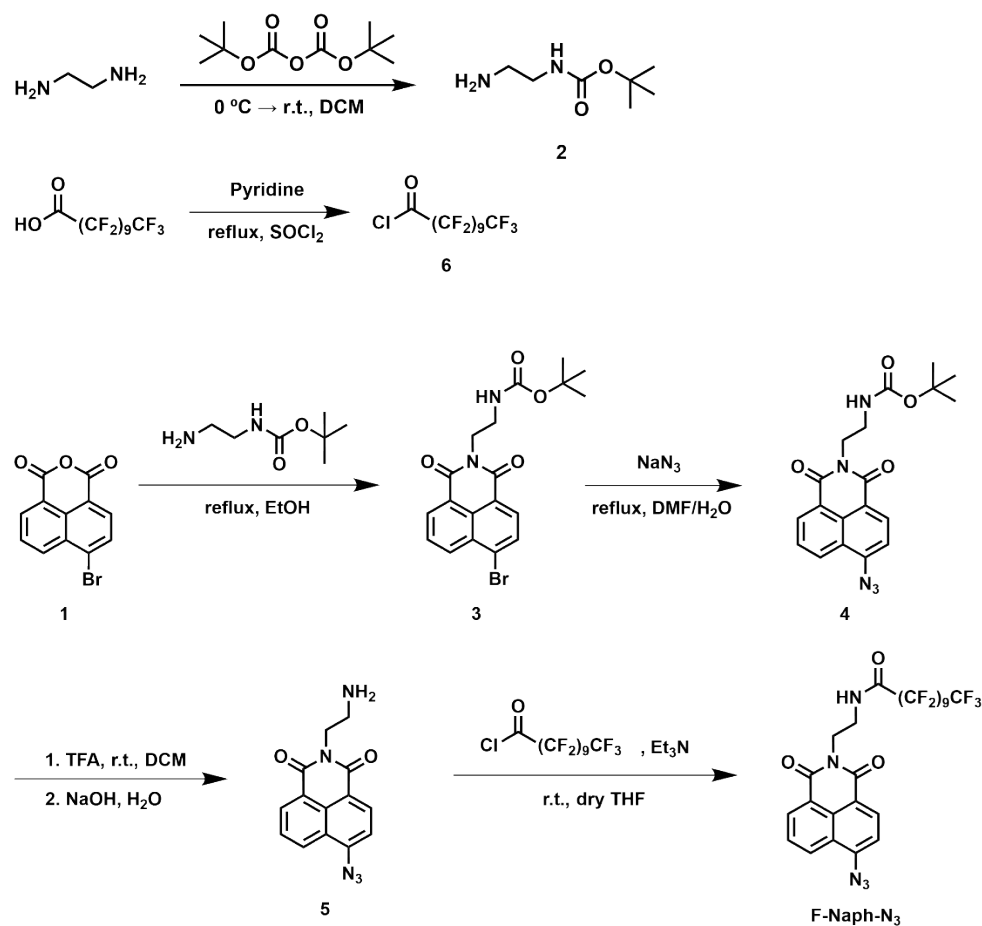
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1. Synthetic procedures



Scheme S1. Reaction scheme illustrating the synthetic procedure for F-Naph-N₃.

Synthesis of 2 [S1]

Ethylenediamine (200 mmol, 13.3 mL) was dissolved in 100 mL of dichloromethane (DCM) and vigorously stirred at 0 °C for 15 min. *di-tert-butyl* bicarbonate was dissolved in 80 mL of DCM and added slowly to stirred solution of ethylenediamine for 3 h. After dropwise, the solution was further stirred for 24 h at room temperature. The solvent was then removed under reduced pressure. The crude product was diluted with H₂O and extracted with DCM. The organic layer was washed with brine, dried over sodium sulfate anhydrous (Na₂SO₄), and concentrated under reduced pressure to afford **2** (1.99 g, 59%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 4.99 (br s, 1H), 3.14–3.18 (q, *J* = 5.6 Hz, 2H), 2.78–2.81 (t, *J* = 6.4 Hz, 2H), 1.42 (br s, 9H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 156.37, 79.35, 43.30, 41.89, 28.52.

Synthesis of 3 [S2]

2 (2.12 g, 13.2 mmol) was dissolved in 25 mL of ethanol (EtOH) and stirred for a few minutes. **1** (3.6 g, 13.0 mmol) was added, and then the reaction mixture was refluxed for 3 h. The reaction mixture was cooled to room temperature. The precipitated solid was filtered, washed with EtOH, and dried under vacuum to afford **3** (4.51 g, 83%) as a white solid. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.58–8.60 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.47–8.50 (d, *J* = 8.8 Hz, 1H), 8.34–8.36 (d, *J* = 7.6 Hz, 1H), 7.97–7.98 (d, *J* = 8.0, 1H), 7.77–7.81 (dd, *J* = 8.0, 7.2 Hz, 1H), 5.01 (br s, 1H), 4.30–4.33 (t, *J* = 11.6, 2H), 3.51–3.52 (m, 2H), 1.27 (br s, 9H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 163.95, 163.93, 156.12, 133.36, 132.22, 131.39, 131.13, 130.57, 130.42, 129.01, 128.11, 122.90, 122.03, 79.22, 40.11, 39.56, 28.29. Melting point: 177–178 °C. HRMS (EI+): *m/z* calculated for C₁₉H₁₉BrN₂O₄+H⁺ [M+H⁺]: 420.0510, found: 420.0515.

Synthesis of 4

3 (1.26 g, 3.0 mmol) was dissolved in 15 mL of dimethylformaldehyde (DMF) and the suspended solution was heated. Sodium azide (0.78 g, 12.0 mmol) was dissolved in 2 mL of water and added slowly to the reaction mixture. The reaction mixture was refluxed for 2 h, dissolved in excess of water and filtered. The residue was dissolved in DCM and washed with brine, dried over Na₂SO₄, and the solvent was evaporated under reduced pressure to give **4** (0.90 g, 79%) as an orange solid. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.62–8.64 (d, *J* = 7.2 Hz, 1H), 8.57–8.59 (d, *J* = 8.0 Hz, 1H), 8.42–8.44 (d, *J* = 8.4 Hz, 1H), 7.72–7.76 (t, *J* = 8.0 Hz, 1H), 7.45–7.47 (d, *J* = 8.0, 1H), 4.95 (br s, 1H), 4.33–4.36 (t, *J* = 6 Hz, 2H), 3.53 (m, 2H), 1.29 (br s, 9H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 164.36, 163.90, 156.12, 143.60, 132.43, 131.92, 129.23, 128.92, 126.90, 124.31, 122.44, 118.71, 114.71, 79.21, 39.94, 39.69, 28.29. Melting point: 131–147 °C. HRMS (EI+): *m/z* calculated for C₁₉H₁₉N₅O₄⁺ [M⁺]: 381.1437, found: 381.1440.

Synthesis of 5

4 (0.85 g, 2.2 mmol) and trifluoroacetic acid (TFA, 1.7 mL, 22.2 mmol) were dissolved in 10 mL of DCM and stirred for 1.5 h at room temperature. The solvent and TFA were removed under reduced pressure and poured into water. A sodium hydroxide solution (1 M) was added into the solution to deprotonate the ammonium salt. The precipitated solid was filtered, and the residue was dissolved in DCM, washed with brine, dried over Na₂SO₄, and the solvent was evaporated under reduced pressure to afford **5** as a brown solid. ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 8.48–8.50 (d, *J* = 7.2 Hz, 1H), 8.42–8.44 (d, *J* = 8.0 Hz, 1H), 8.37–8.39 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.82–7.86 (t, *J* = 8.0 Hz, 1H), 7.70–7.73 (d, *J* = 8.4 Hz, 1H), 4.02–4.05 (t, *J* = 6.4 Hz, 2H), 2.77–2.81 (t, *J* = 7.6 Hz, 2H), 1.60 (br s). ¹³C NMR (100 MHz, DMSO-*d*₆, δ, ppm): 163.39, 162.95, 142.62, 131.44, 131.35, 128.29, 128.16, 127.21, 123.43, 122.25, 118.28, 115.84, 42.71 (one peak in aminoethyl was not observed due to the solvent peak). Melting point: 116–125 °C. HRMS (EI+): *m/z* calculated for C₁₄H₁₁N₅O₂⁺ [M+H⁺]: 282.0985, found: 282.0984.

2. Supplementary figures

UV/Vis spectra

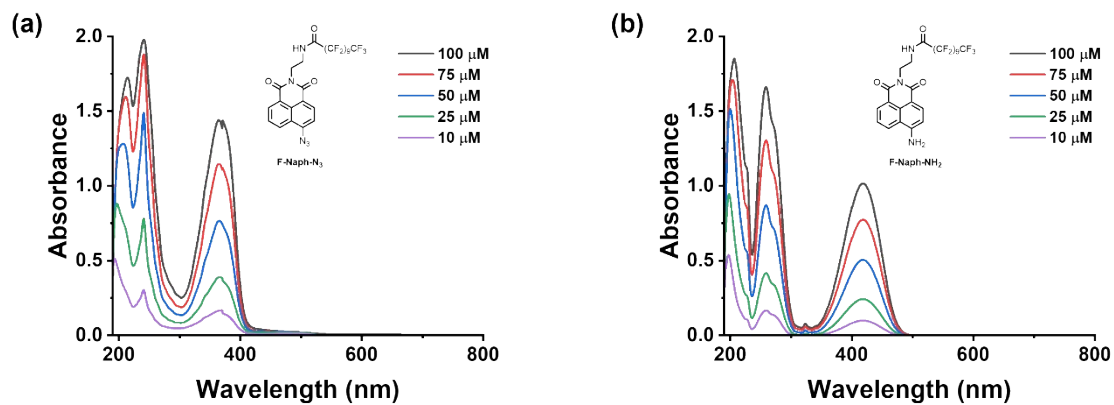


Figure S1. UV/Vis spectra for (a) F-Naph-N₃ and (b) F-Naph-NH₂ in acetonitrile (ACN).

Titration for H₂S in solution

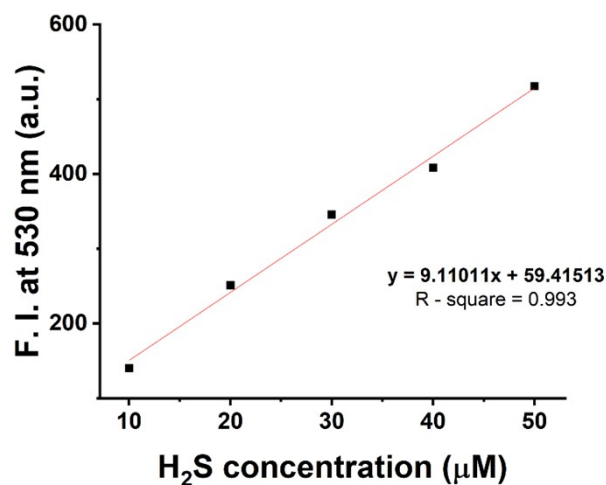


Figure S2. Plot of fluorescence intensity at 530 nm of solution containing F-Naph-N₃ (20 μM) with various concentrations of H₂S in an ACN/H₂O solution (v/v = 6:4, pH 8.0 sodium phosphate buffer 10 mM) after 1 h. [PMT: 580 V, Slit: 5 nm]

The quenching effect of copper nitrate as a H₂S scavenger

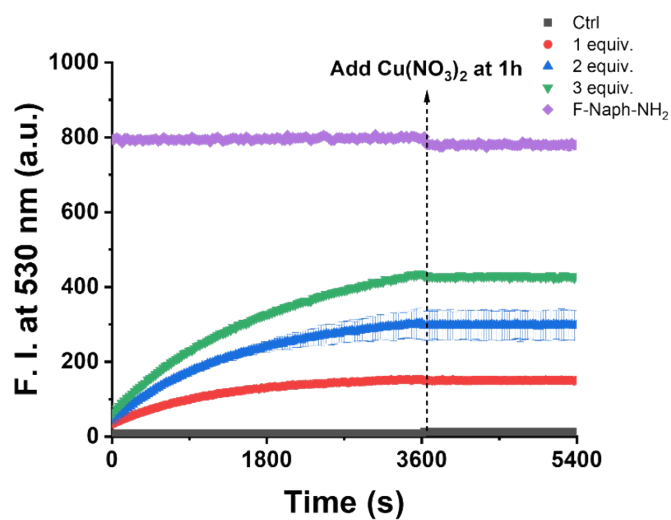


Figure S3. Time-dependent fluorescence intensity of F-Naph-N₃ (20 μM) at 530 nm with the different concentrations of H₂S (1, 2, and 3 equiv.) in an ACN/H₂O solution (v/v = 6:4, pH 8.0 sodium phosphate buffer 10 mM), and subsequent measurement after the addition of copper(II) nitrate trihydrate (2 equiv. of added H₂S) at 1 h. [PMT: 580 V, Slit: 5 nm]

F-Naph-N₃ treated by H₂S on PTFE membrane

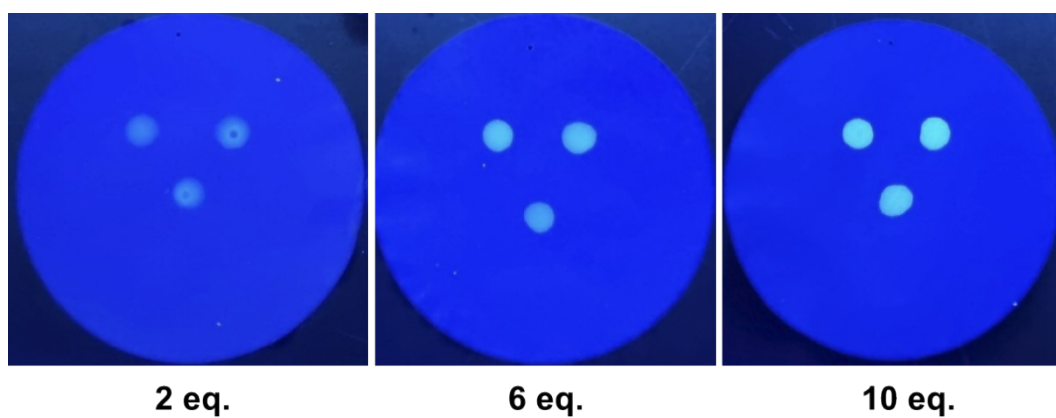


Figure S4. The fluorescence of F-Naph-N₃ treated by H₂S on polytetrafluoroethylene (PTFE) membrane filter under the hand-held UV lamp (365 nm).

Titration for H₂S in fluorosolid-phase extraction (F-SPE) application

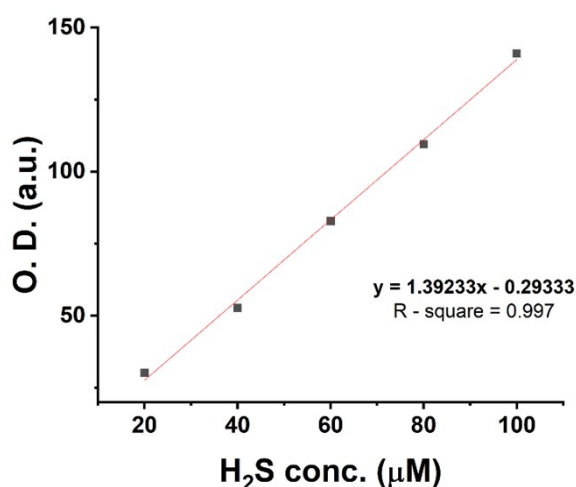


Figure S5. Plot of fluorescence intensity (optical density) of F-Naph-N₃ (20 μM) treated by various concentrations of H₂S in F-SPE process. The solution was incubated for 1 h in an ACN/H₂O solution ($v/v = 6:4$, pH 8.0 sodium phosphate buffer 10 mM) before spotting onto polytetrafluoroethylene (PTFE) membrane filter.

Fluorescence measurements in dyeing solutions

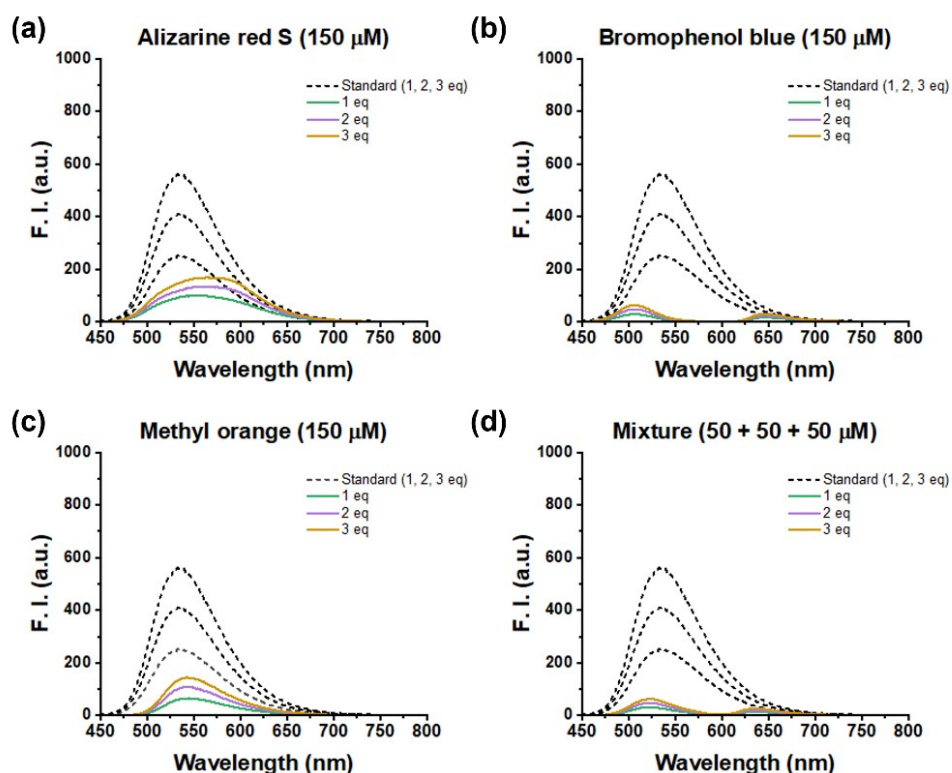


Figure S6. Fluorescence emission spectra of F-Naph-N₃ (20 μM) with the different concentrations of H₂S (20, 40, and 60 μM) in an ACN/H₂O solution ($v/v = 6:4$, pH 8.0 sodium phosphate buffer 10 mM) containing 150 μM of (a) alizarine red S, (b) bromophenol blue, (c) methyl orange, and (d) their mixture (50 μM of each dyes) after the incubation for 1 h. Dashed spectra represent the emission spectra in standard curve (Fig. 1d). [PMT: 580 V, Slit: 5 nm]

NMR spectra

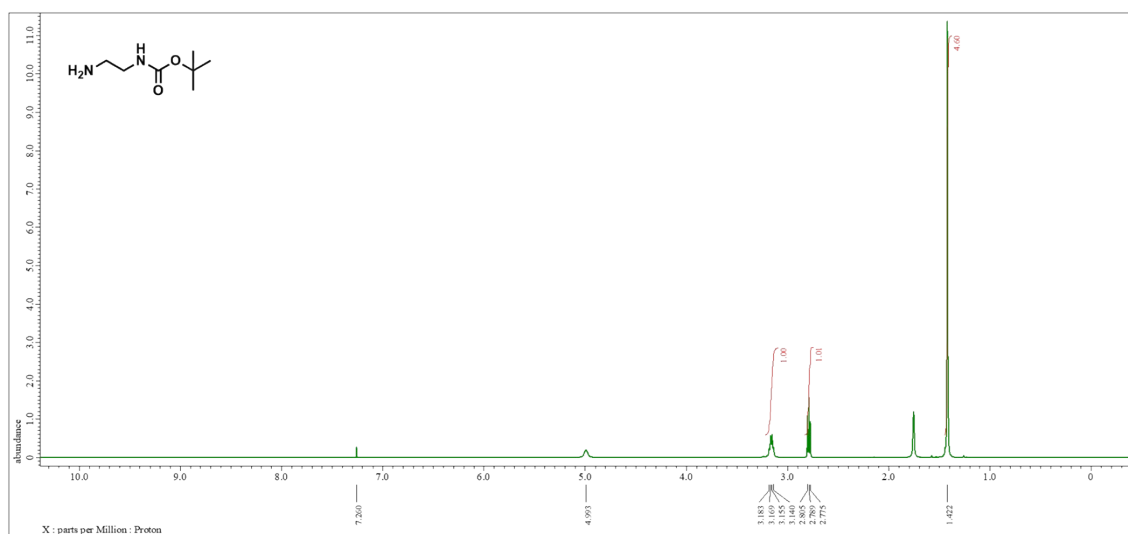


Figure S7. ¹H NMR spectrum (400 MHz, CDCl₃) of 2.

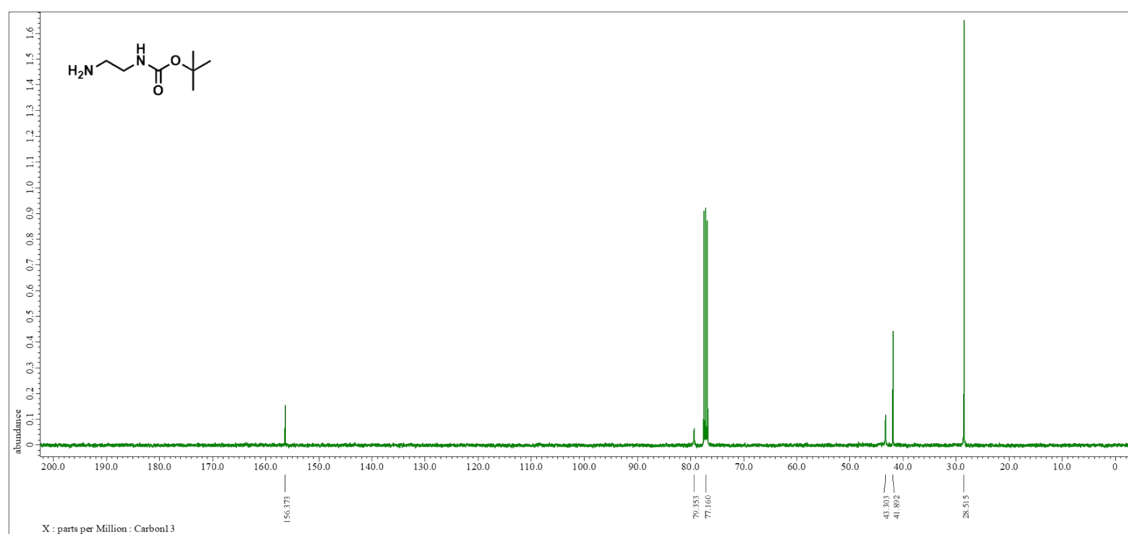


Figure S8. ¹³C NMR spectrum (100 MHz, CDCl₃) of 2.

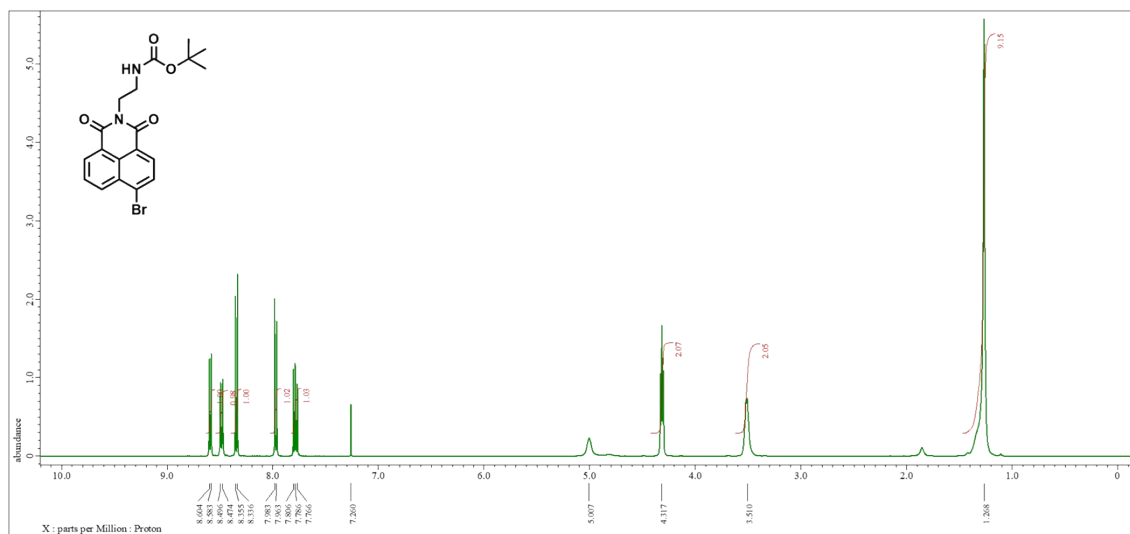


Figure S9. ¹H NMR spectrum (400 MHz, CDCl₃) of 3.

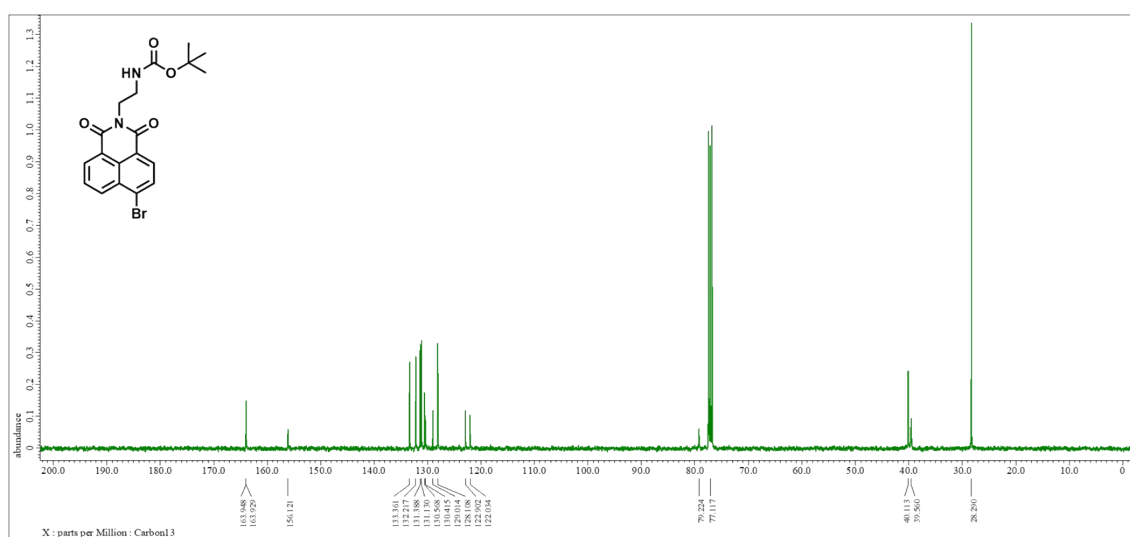


Figure S10. ¹³C NMR spectrum (100 MHz, CDCl₃) of 3.

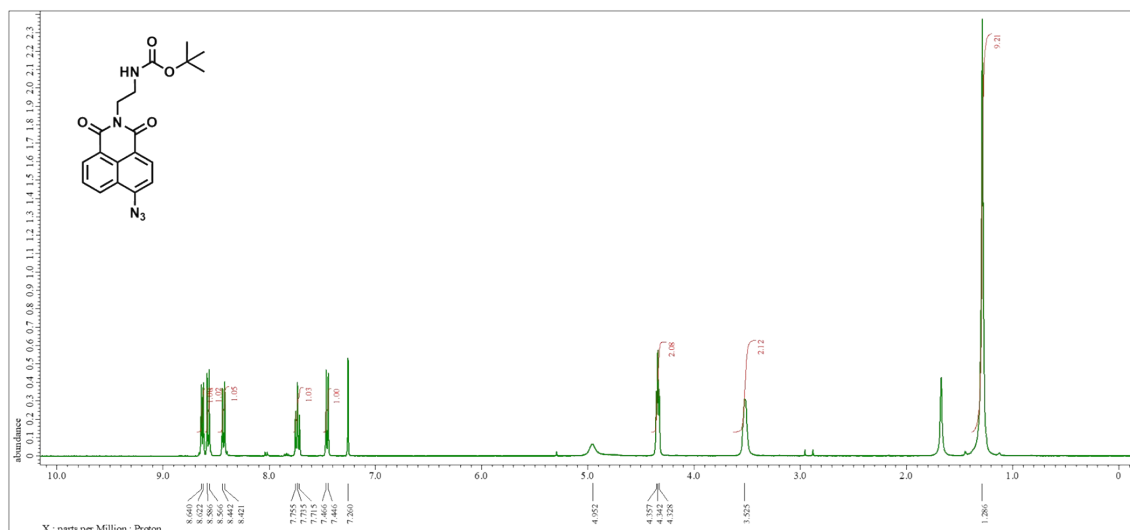


Figure S11. ¹H NMR spectrum (400 MHz, CDCl₃) of 4.

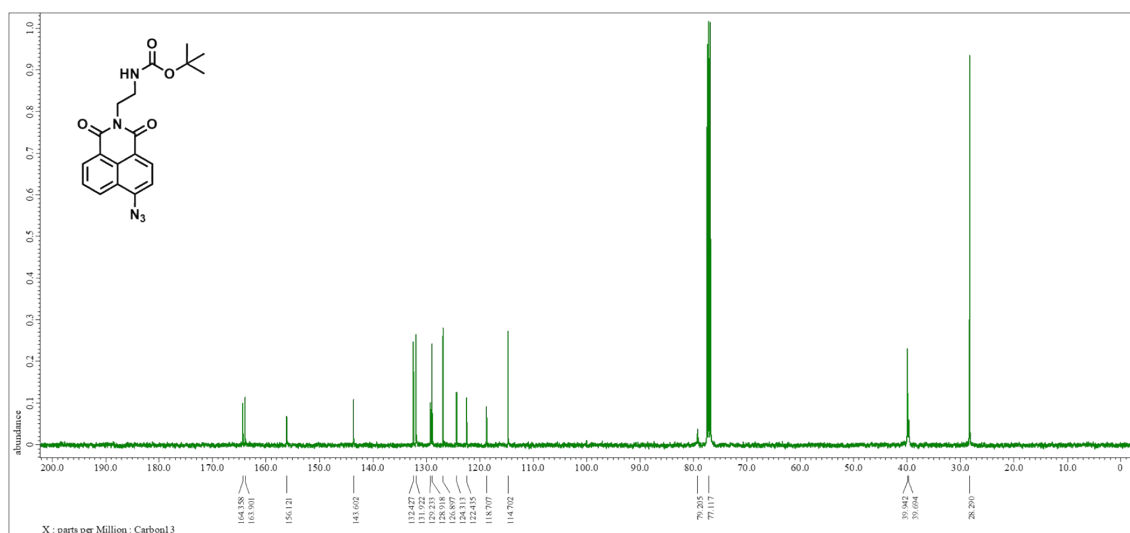


Figure S12. ¹³C NMR spectrum (100 MHz, CDCl₃) of 4.

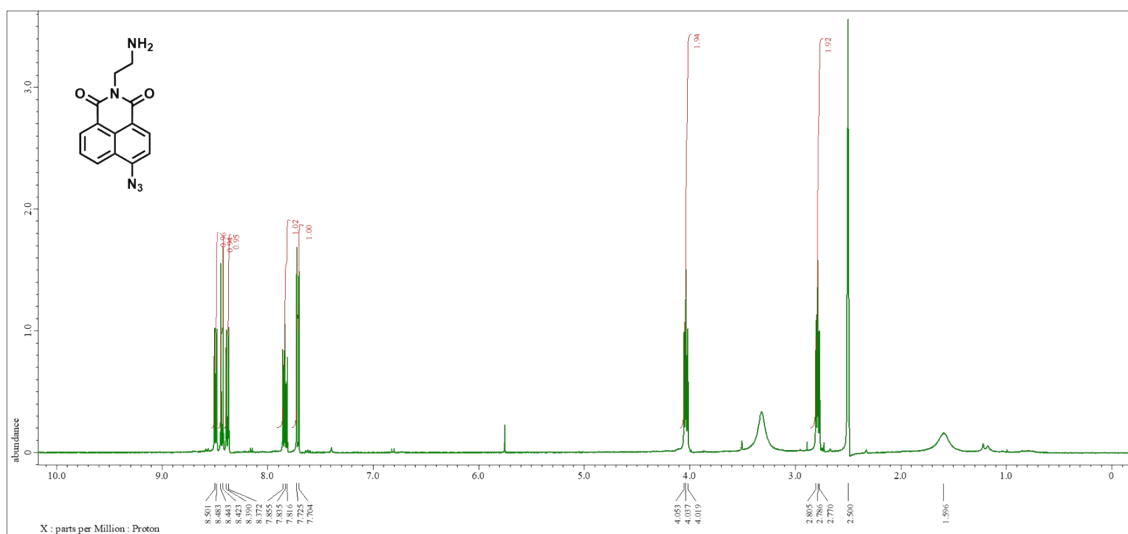


Figure S13. ^1H NMR spectrum (400 MHz, $\text{DMSO}-d_6$) of 5.

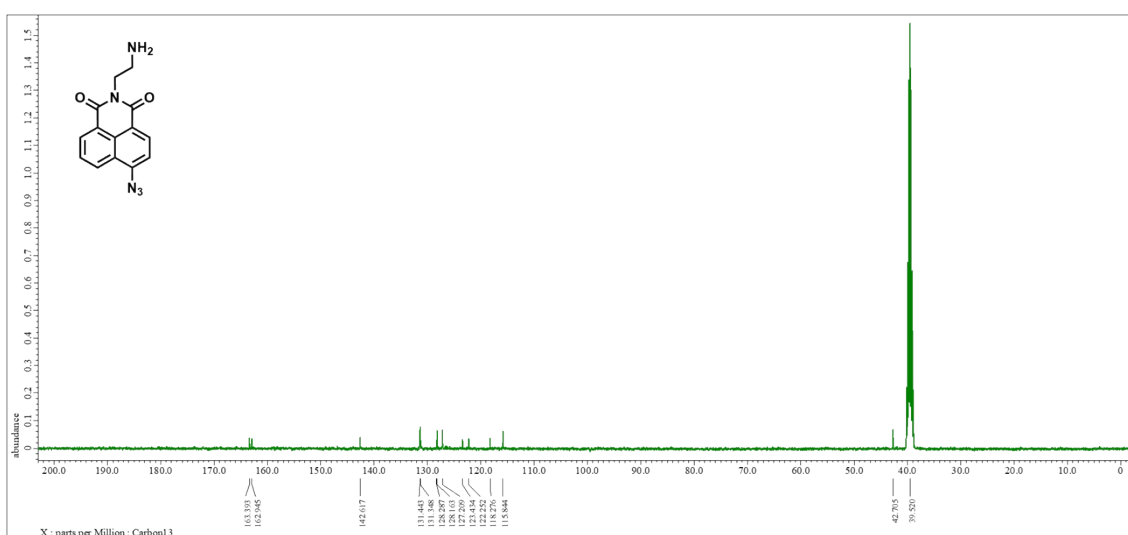


Figure S14. ^{13}C NMR spectrum (400 MHz, $\text{DMSO}-d_6$) of 5.

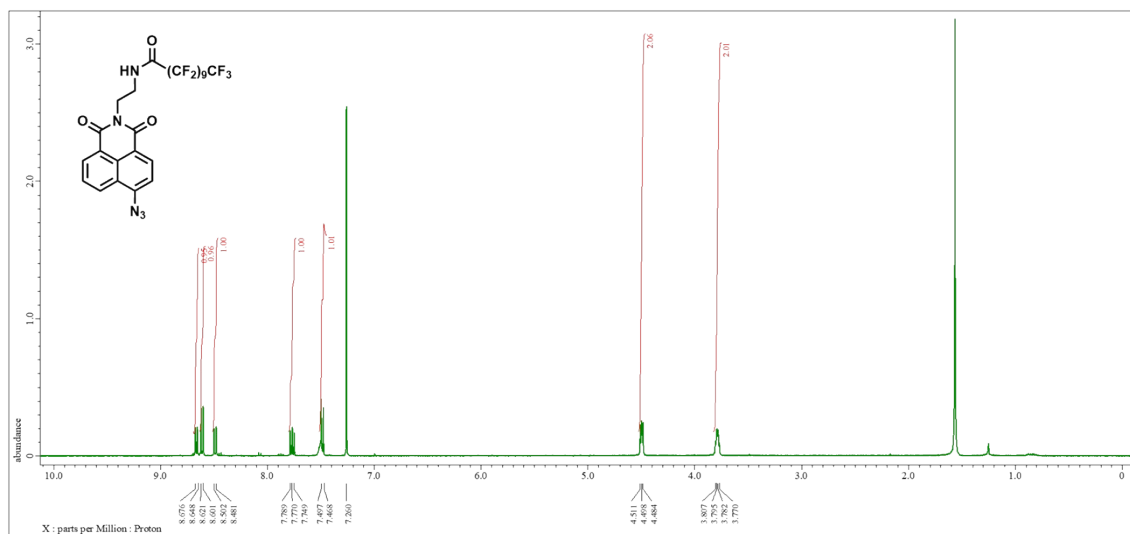


Figure S15. ^1H NMR spectrum (400 MHz, CDCl_3) of F-Naph- N_3 .

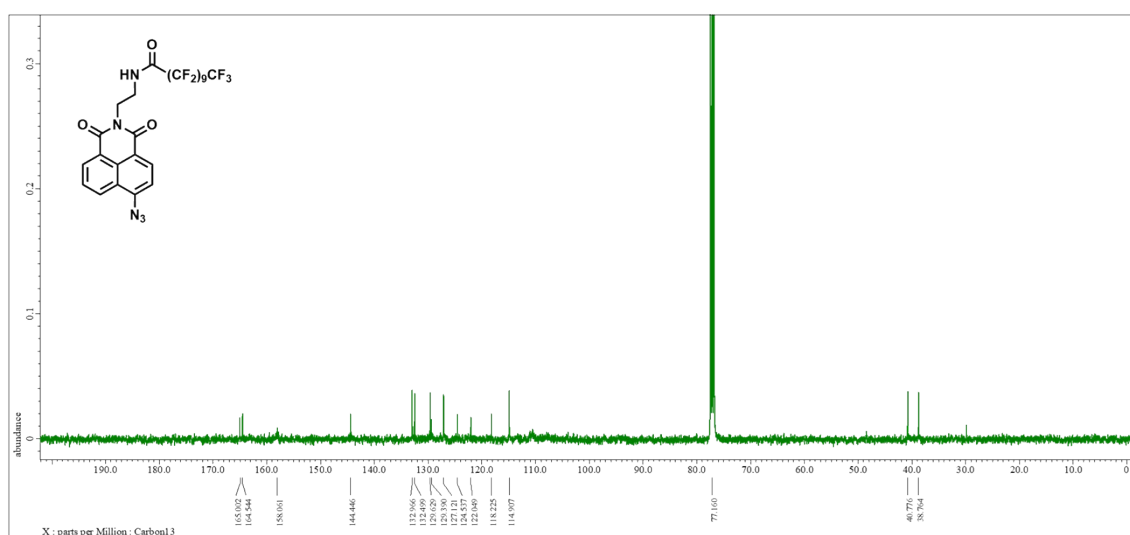
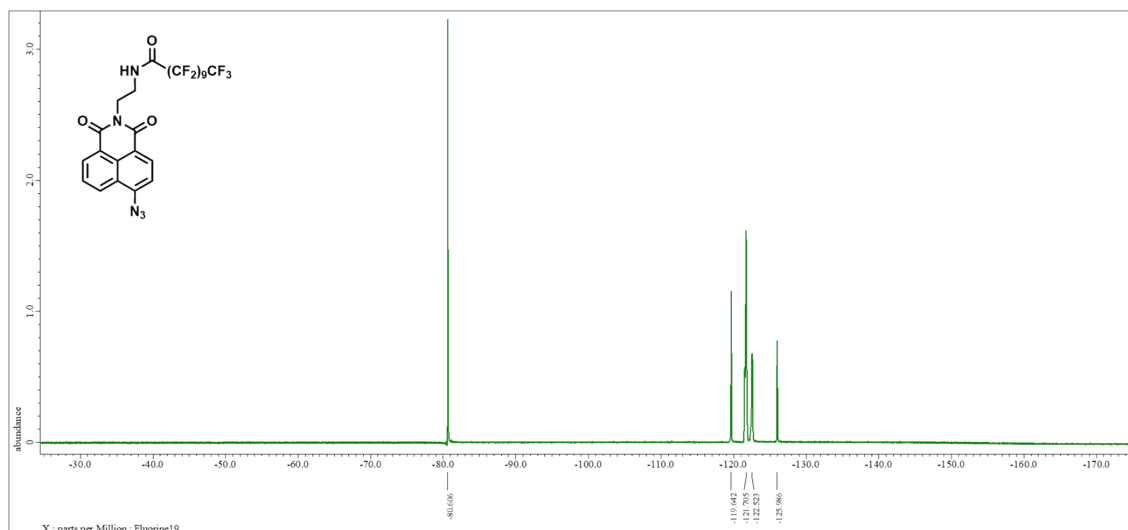
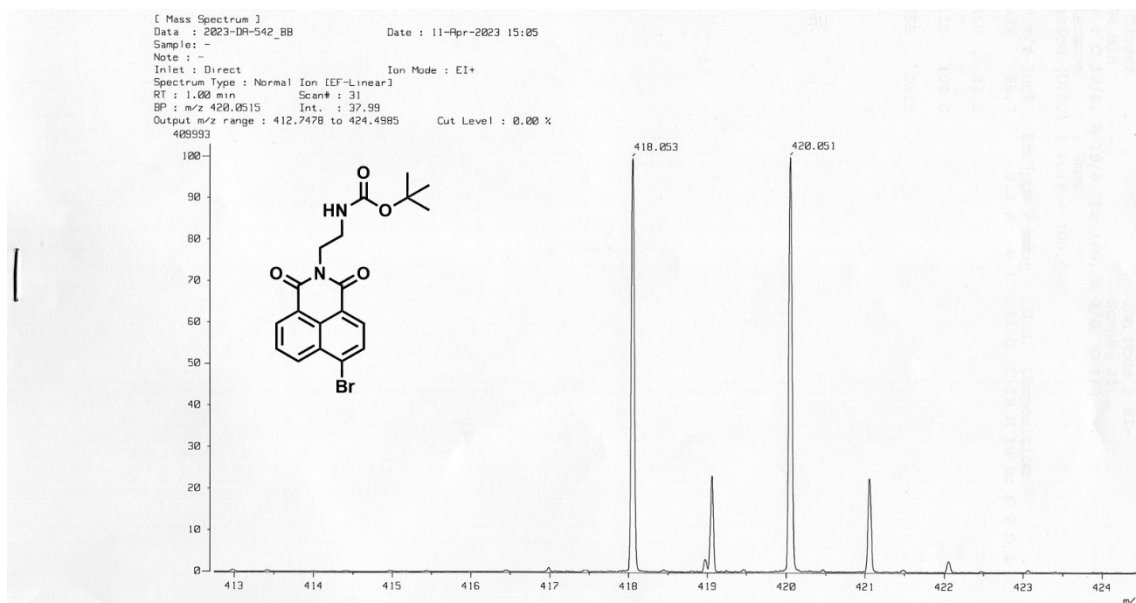


Figure S16. ^{13}C NMR spectrum (100 MHz, CDCl_3) of F-Naph- N_3 .



High-resolution mass spectra



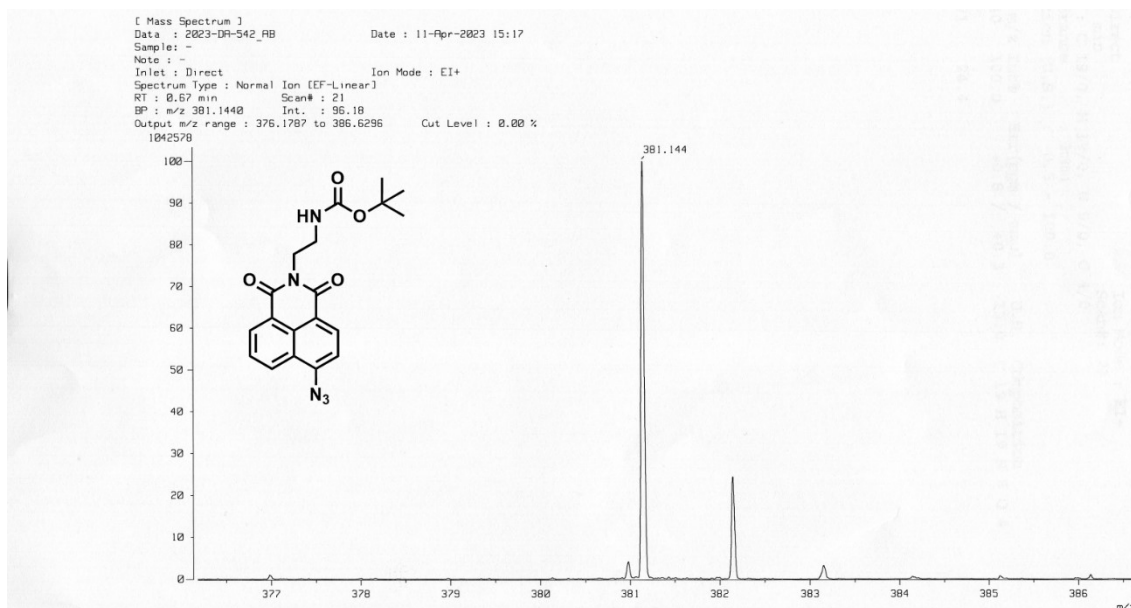


Figure S19. High-resolution mass spectrum (EI+) of 4.

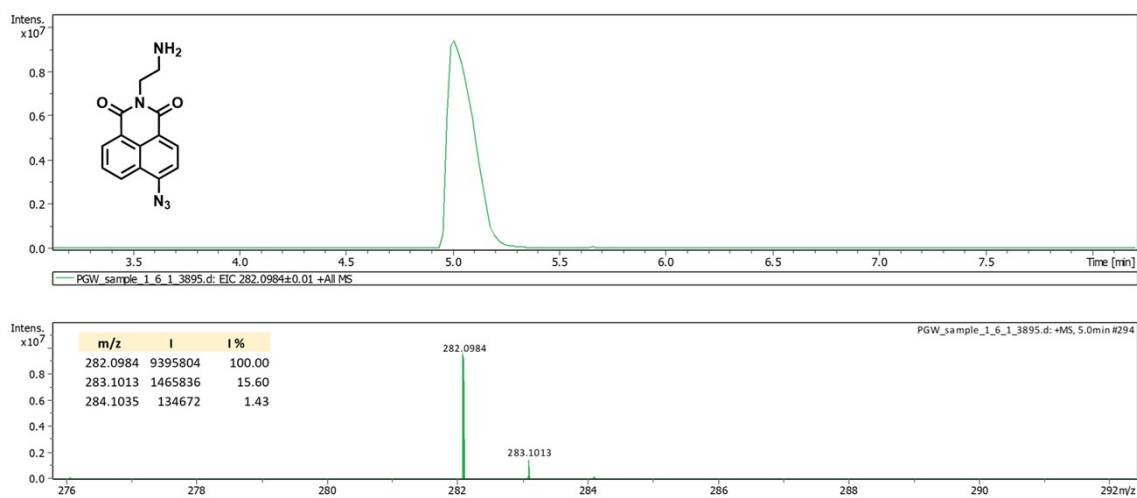


Figure S20. High-resolution mass spectrum (EI+) of 5.

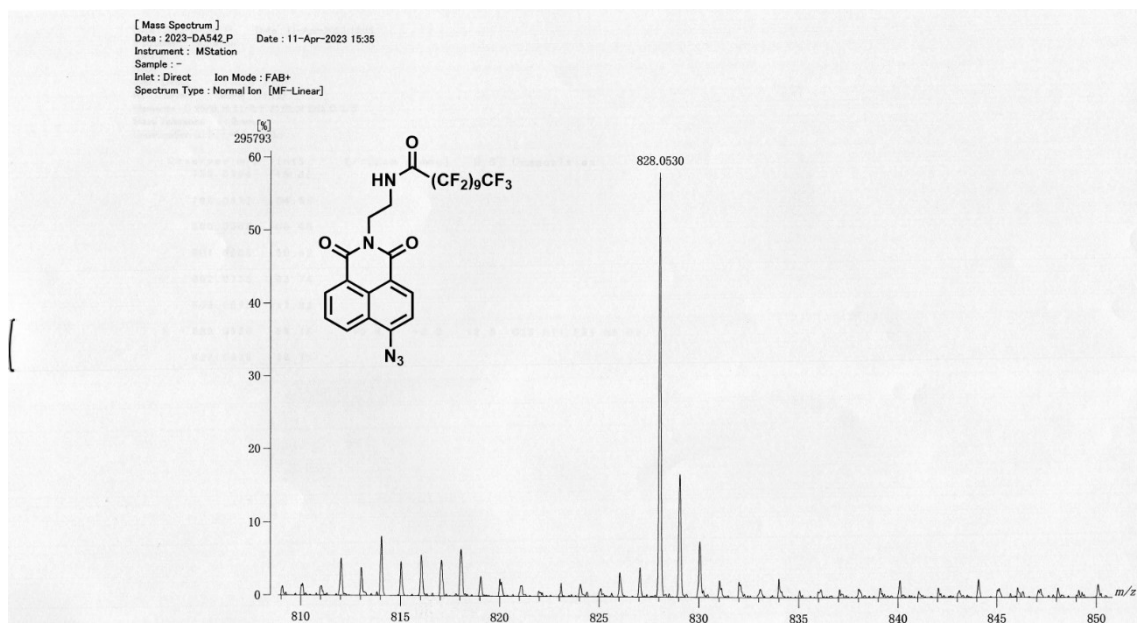


Figure S21. High-resolution mass spectrum (FAB⁺) of F-Naph-N₃.

3. References

[S1] M. D. McKenna, I. Grabchev and P. Bosch, *Dyes Pigment.*, 2009, **81**, 180–186.

[S2] X. Zhou, F. Su, H. Lu, P. Senechal-Willis, Y. Tian, R. H. Johnson and D. R. Meldrum, *Biomaterials*, 2012, **33**, 171–180.